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Dedicated to the 110th anniversary of M.I. Kabachnik's birth

Synthesis, Transport, and Ionophoric Properties of α,ω-Diphosphorylated Azapodands: XI.[1] Membrane Transport of Metals by Phosphorylated Diazapodands

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Abstract—The membrane transport of rare-earth metals and scandium by new diphosphorylated diazapodands was studied. It was found that the introduction of butyl groups and an additional phosphoryl group on the nitrogen atoms of the terminal aminomethylphosphinoyl groups of azapodands decreases the efficiency of transport of rare-earth metals and increases the selectivity to scandium ion.

Keywords: phosphorylated diazapodands, membrane transport, rare-earth metals, scandium

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Phosphorylated podands and azapodands are effective and selective complexing agents for the use as extractants and membrane carriers [2–5]. We previously observed a highly efficient membrane transport of a number of metal ions by lipophilic phosphorylated diamines and azapodands containing long-chain alkyl substituents on the phosphorus atom and alkylene bridges between the terminal aminophosphoryl moieties [4]. In the present paper we report the results of our study of the membrane transport properties of new diphosphorylated diazapodands containing *p*-tolyl substituents on the phosphorus atom and polyether linker of the general formula $[(4\text{-}CH_3C_6H_4)_2P(O)CH_2NR]_2Z$, where R = H, Z = $(CH_2)_2OCH_2CH_2O(CH_2)_2$ (**1**); R = C_4H_9, Z = $(CH_2)_2OCH_2CH_2O(CH_2)_2$ (**3**); R = $(4\text{-}CH_3C_6H_4)_2P(O)CH_2$, Z = $(CH_2)_2OCH_2CH_2O(CH_2)_2$ (**2**); R = H, Z = $(CH_2)_3OCH_2CH_2O(CH_2)_3$ (**4**), with respect to some rare-earth metals [Nd(III), Sm(III), and Gd(III)], as well as scandium. The resulting data on transport flows are listed in Table 1.

To evaluate the contribution of noninduced membrane transport (blank run), we determined the transport flows of metals through the membrane impregnated by the membrane solvent 1,2-dichlorobenzene (J_0) and to reveal much lower (by 1–2 orders of magnitude) transport flows of all the substrates in this case.

According to the obtained results, the highest transport flows are characteristic of the structurally similar carriers **1** and **4**. Therewith, it can be noticed that the length of the polyether chain only slightly affects the transport flows of rare-earth metal ions. However, in going from carrier **1** to carrier **4**, the Sc(III) flow increases more than 4.5-fold. The subsequent modification of the aminophosphoryl core in **1** (additional butyl substitution) decreases the transport flows of all the metals, except for the small Sc(III) ion, with carrier **2**. Being a weak electron-donor substituent, butyl should slightly increase the electron density on the nitrogen atoms, thereby favoring stronger binding of metal substrates with these coordination centers and, therefore, decreasing metal flows are likely to be associated with steric hindrances to the formation of the transport complexes of rare-earth metals, whereas the smaller Sc(III) easier enters the host's pseudocavity.

The introduction of the second electron-acceptor methylenephosphoryl group on the nitrogen atoms in

[1] For communication X, see [1].